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SOLVOLYTIC DEGRADATION OF POLYMERIC PROPELLANT BINDERS

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Prepared for:

Naval Sea Systems Command

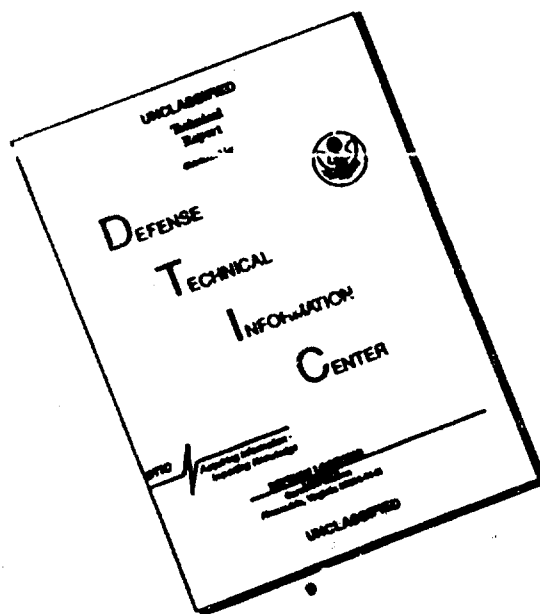
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SOLVOLYTIC DEGRADATION OF POLYMERIC
PROPELLANT BINDERS

Final Report

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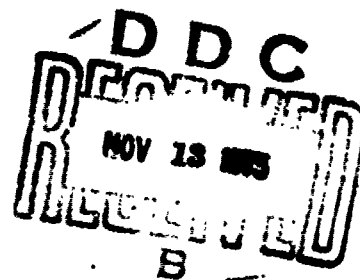
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I. Glossary of Symbols

AP.....	Ammonium Perchlorate
BCMB.....	1,4-Bis-(chloromethyl)benzene
Butarez CTLI.....	Carboxy-terminated polybutadiene
EDA.....	Ethylenediamine
Epon 812.....	Diglycidyl ether of bisphenol-A
HEM.....	High energy material
HMDS.....	Hexamethyldisilazene
MAPO.....	Tris(2-methylaziridinyl-1)phosphine oxide
NOL.....	Naval Ordnance Laboratory
pKa.....	Negative logarithm of the acidic ionization constant
TDI.....	Toluene diisocyanate
Tg.....	Polymer glass transition temperature

II. Abstract

The effect of various catalysts on the rate of solvolysis of the polyester and polyurethane binders in butylamine was studied; Bismuth nitrate, lead acetate trihydrate, zirconyl nitrate dihydrate, ammonium salts, 1,4-bis(chloromethyl)benzene and tautomeric catalysts such as 2-hydroxypyridine, 1,2,4-triazole and pyrazole were found to decrease the time of dissolution of the polyester binders III at room temperature by at least fifty percent; zinc acetylacetonate had a similar accelerating effect on the polyurethane binder II; ammonium chloride, triazole, pyrazole and imidazole also decreased the dissolution time of the polyurethane binder IV by fifty percent. The degradation of four polymeric rocket propellant binders with hexamethyldisilazine (HMDS) has been studied and this method shows limited success. A model binder linear polyurethane of known intrinsic viscosity was prepared and successfully photolytically degraded in benzene. Liquid ammonia was found to degrade binders I, III and IV at 50°. A model rocket fuel containing ammonium chloride instead of ammonium perchlorate was prepared and found to solvolytically degrade in liquid ammonia to give an 84% recovery of the ammonium chloride. Methanol was shown to be a suitable solvent for the extraction of the nitro and hydrocarbon plasticizers from the polyurethane and polyester binders.

III. Introduction

Polymer binders in propellants usually constitute from 15 to 20% of the total weight of the propellant. The remaining 84-80% is generally made up of oxidizer, usually (in Polaris motors) ammonium perchlorate (AP) 60-82%, aluminum metal, 2-18%, and stabilizers, 0-1%. The binders of chief concern at present (in Polaris motors) appear to be one of two types: (1) polyurethanes or (2) cured polybutadiene prepolymers. The problem of disposing of obsolete propellants is a formidable one because of the legal limitations on burning and dumping. The product gases from burning would cause serious pollution of the atmosphere and other possible means of disposal also present problems.

The most desirable means of disposal would involve separation of the binder, oxidizer and metal by suitable physical or mechanical processes which would permit their reuse. Such a procedure may also offer important economic advantages, particularly if recovery of each component could be accomplished in reasonable purity. The problems associated with processes directed toward mechanical separation of the components are many. The polymeric binder is a cross-linked material so that it is not soluble, making it impossible to remove the binder simply by solvent extraction. The properties of the binder are similar to those of vulcanized rubber. Furthermore, the finely divided metal and oxidizer particles are intimately coated with the binder, which is impervious to water, making it impossible to remove the water-soluble oxidizer from the metal and binder.

The chemical nature of the binder is such that a reasonable approach appeared to be a chemical one. This chemical approach would involve cleavage of the polymeric cross-links leaving binder fragments which now would be soluble in a suitable solvent. This would permit the binder to be removed from oxidizer and metal by a simple extraction-filtration procedure.

IV. Background Information

As pointed out in Section II, the binders of chief concern are either polyurethanes or cured carboxy-terminated polybutadiene prepolymers. The crosslinks are of the ester type and susceptible to cleavage by several chemical approaches.

A. Polyurethanes

Three general methods have been mentioned as possible means to degrade polyurethanes:

(1) Hydrolytic cleavage

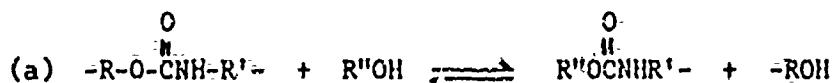
Although the urethane link is an ester-like link, it is more stable to hydrolysis than esters; however, it is subject to both acidic and basic hydrolysis. Generally, strong acid or strong base is necessary to accomplish hydrolysis at a reasonable rate. Unfortunately, AP is converted to free ammonia and perchlorate ion in presence of strong base and to perchloric acid and ammonium ion in presence of strong acid. This limits the use of a hydrolytic reaction for degradation to weak bases and acids, particularly if recovery of AP is a prime objective. Indeed, recently it has been disclosed [1] that hydrolytic breakdown and dissolution of many propellants can be carried out with surprising ease in 600 g scale with subsequent recovery of constituents in high yield. The approach involves treating the propellant composites with either hydrochloric acid or ammonium hydroxide at elevated temperature.

(2) Thermal degradation

Polyurethanes derived from primary and secondary alcohols generally require temperatures above 200°C before thermal degradation occurs at an appreciable rate. Those derived from tertiary alcohols and phenols undergo thermal degradation at a lower temperature, as low as 50°C [2]; however, it appears that the latter are seldom used in the binders under consideration. Thermal means of degradation, therefore, appear to be impractical, particularly in presence of the large amount of oxidizer (AP).

(3) Solvolytic cleavage

The urethane link is cleaved by (a) alcohols and (b) amines (including ammonia):

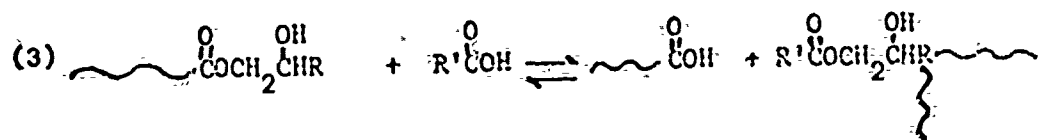
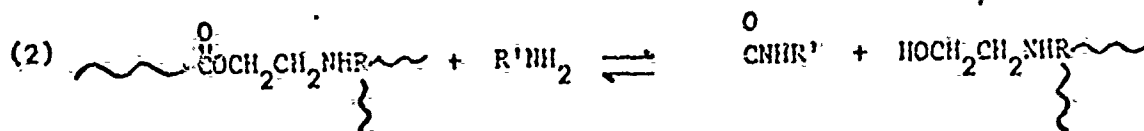
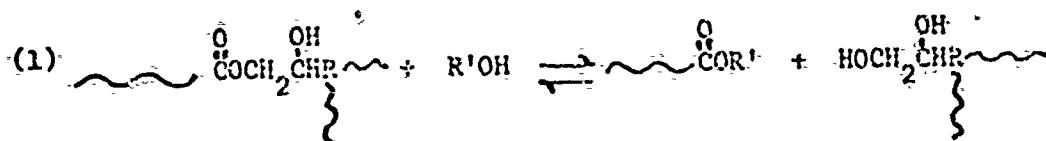


Since polyurethane binders are synthesized from a mixture of dihydroxy and trihydroxy compounds, the use of ammonia, primary and secondary amines or alcohols should accomplish a chain cleavage for each molecule which reacts. Sufficient reaction would cleave all crosslinks and the remaining polymer would then be soluble in a suitable solvent. Indeed, it has been found that ammonia and primary amines are useful for solvolyzing polyesters binders at moderate temperature [?].

B. Polyesters

Since the polybutadiene based binder matrices are extensively crosslinked, there is little possibility that solvents alone could be used to remove them from the oxidizer and metal. The most vulnerable link in this matrix is the ester link which is known to be hydrolyzable through either acid or base catalysis to the corresponding alcohol and carboxyl group. Such hydrolytic reactions would also cleave the crosslinks and leave the liquid prepolymer of 2000-4000 molecular weight. (Some crosslinking may have occurred between these prepolymer chains through oxidation processes on the carbon-carbon double bonds of the chain). However, the problem of recovery of AP almost precludes the use of strong acid or strong base to hydrolyze the matrix. Thermal degradation of these matrices also appear not to be feasible in the propellant form due to potential hazard from rapid oxidation.

The most feasible method of degradation, similar to that of the polyurethanes, appears to be based upon a depolymerization-termination reaction utilizing monofunctional alcohols, ammonia, amines or carboxylic acids. These equilibria are shown in the following equations:



V. Samples

Sample	Description
NOL Sample I: Polyethyleneglycol, trisethylolpropane, toluene diisocyanate	Plasticized with a 1:1 eutectic of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)- acetal (75 wt. % of binder)
NOL Sample II: Hydroxy-terminated butadiene, toluene diisocyanate	Unplasticized and plasticized with hydrocarbon oil (50 wt. % of binder)
NOL Sample III: Butarex CTL-I* NAFO,**Epon 812***	
NOL Sample IV: Polyethyleneglycol, trisethylolpropane, nitrozo diisocyanate	Plasticized with a 1:1 eutectic of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)- acetal (50 wt. % of binder)

VI. Experimental

Previous work [4] has demonstrated the feasibility of using primary amines at temperatures below 100° to dissolve polyurethane and polyester propellant binders. However, due to the potential hazards of heating together the oxidizing and reducing agents present in the actual propellants it was desirable to degrade the binders at as low a temperature as possible. With this objective in mind a study was made of various compounds capable of catalyzing the solvolysis of polyesters and polyurethane propellant binders in butylamine at low temperatures. Metal salts, quaternary ammonium salts, amines and bifunctional or tautomeric compounds were considered. The use of cosolvents was also investigated.

Effect of Various Catalysts on the Solvolysis of Polyester and Polyurethane Binders in n-Butylamine.

The following catalysis studies were centered on NOL sample III using one-quarter inch cubes (approximately 0.25 g each) of the polyester in 25 ml of n-butylamine at room temperature.

In an initial study a number of possible catalysts were used and the following dissolution times were observed. (Table I):

Catalysis of the aminolysis and the alcoholysis of esters [5], as well as the catalysis of urethane formation [6], has been extensively studied. It was therefore thought that this information could be used to obtain information about the kinetics and the ease of polyester and polyurethane solvolysis at low (20-50°) temperatures. It was also hoped that it would be possible to relate the solvolysis of both carbonyl-containing polymers to each other. Since metal salts, particularly those of lead, zinc and manganese have been used in the

*Carboxyterminated polybutadiene, **Tri(2-methyl aziridinyl)-phosphine oxide, ***Diphenyl ether of bisphenol-A

TABLE I

Catalyst, 1 g	Time (hours)
Control	14
Bismuth nitrate	7 3/4
Lead nitrate	9
Dibutyltin dilaurate	9 1/2
Ferrous ammonium sulfate	11
Disodium hydrogen phosphate	11 1/2
Sodium nitrate	13
Ammonium molybdate	13
Triethylamine	13 3/4
Potassium oxalate	>15
Triethylenediamine	>16
Zinc acetonylacetate	>15

alcoholysis of polyesters at elevated temperatures, these were studied first. The results of this study, summarized in Table II, shows a number of metal salts capable of catalyzing the solvolysis.

TABLE II

Metal Salt (1 g)	Time(hrs)	Remarks
Control	14	
Lead acetate trihydrate	6 3/4	[7, 8, 9]
Zirconyl nitrate dihydrate	7	
Stannous octoate	8	
Cobalt caproate	8 1/2	as per [13]
Lead stearate	9 1/2	
Lithium chloride	9 1/2	[10]
Zinc acetate dihydrate	9 1/2	[7, 8, 11]
Ferric ammonium sulfate 12 H ₂ O	11 1/2	[7]
Sodium tungstate	13 1/2	[12]
Mercuric oxide	>14	
Manganese chloride	obscured	[8] black soln.
Manganese acetonyl acetate	10	
Vanadyl acetonyl acetate	10-11 obscured	
Dipyridyl methane	13	

Dissolved ammonium salts in butylamine have also been used to catalyze the solvolysis of esters [14, 15]. In an initial attempt triethylamine and acetic acid were added to butylamine; some catalysis was noted. Then, one gram each of various ammonium salts were added to twenty-five milliliters of butylamine. The resulting mixtures were then mixed until dissolution of the salts was noted and the evolution of ammonia had ceased; the rubber samples were then added.

TABLE III

Ammonium salt	Time(hr)	Remarks
Control	14	
1 g 3:1 Et ₃ N/acetic acid	10	[15]
10 g 3:1 Et ₃ N/acetic acid	nr	no butylamine present
1 g Ammonium chloride	6 1/2	
1 g Ammonium bromide	8	
2 g Ammonium bromide	9	
1 g Ammonium iodide	9	
1 g Ammonium thiocyanate	11 1/2	
1 g Ammonium benzoate	7	
1 g Ammonium dihydrogen phosphate	14 1/2	
1 g Tetra-n-butylammonium perchlorate	14	[16]

A run was then made with equimolar amounts of ammonium salts (based on 1 gram, or 0.0187 mole, of ammonium chloride).

TABLE IV

Ammonium salt	Time(hr)
1 g Ammonium chloride	6 1/2
1.44 g Ammonium acetate	7 1/4
2.60 g Ammonium benzoate	7 1/2
1.83 g Ammonium bromide	10
1.49 g Ammonium nitrate	7 3/4
1.42 g Ammonium thiocyanate	9 1/2 (with residue)
2.71 g Ammonium iodide	10
0.5 g Ammonium chloride + 0.72 g Ammonium acetate	7 1/4

The catalytic effect of equimolar concentrations of various butylammonium salts follows the reported [16] order except for the downward displacement of the bromide in the series: $\text{Cl}^- > \text{OAc}^- > \text{Br}^- > \text{NO}_3^- > \text{SCN}^- > \text{Br}^- > \text{I}^-$. Since synergistic catalysis effects are well-known (as in the synthesis of polyurethanes [17]), an attempt was made to catalyze the solvolysis of the polyester with a mixture of ammonium chloride and ammonium acetate (last line in Table IV); no such synergism is apparent.

Since various studies have involved the reaction of esters with amines in alcoholic [10, 18] or other polar solvents [5, 15], such a series was run.

TABLE V

Mixture	Time (hr)
Control	14
1 g NH_4Cl /20 ml BuNH_2 + 5 ml CH_3OH	11 1/2
1 g NH_4Cl /12 ml BuNH_2 + 12 ml CH_3OH	>24
1 g NH_4Cl /5 ml BuNH_2 + 20 ml CH_3OH	>24
2 g NH_4Br /12 ml BuNH_2 + 12 ml BuOH	>14
2 g NH_4Br /20 ml BuNH_2 + 5 ml BuOH	12 (with residue)
12 ml BuNH_2 + 12 ml acetonitrile	>24
12 ml BuNH_2 + 16 ml BuOH	>1 week

The general effect of adding alcohol or polar solvents appears to be a slowing down of the dissolution rate, except in the two cases where only small amounts of alcohol (5 ml) were present.

To determine whether the results shown in Tables III and IV were unique for dissolved ammonium salts, a run was made using corresponding sodium salts in butylamine (again on the basis of 1 gram of ammonium chloride). Although no effect was expected, a moderate effect was observed:

TABLE VI

Sodium salt	Time (hr)
1.1 g Sodium chloride	14
1.53 g Sodium acetate	12 1/2
1.92 g Sodium bromide	9 1/2
1.53 g sodium nitrate	13
2.80 g sodium iodine	10 1/2 (with residue)

Pursuing the thought that dissolved quaternary ammonium salts might be involved in an acid-catalysis type of solvolytic reaction, benzyl chloride and 1,4-bis(chloromethyl)benzene were used, with and without other amines, in butylamine solution.

TABLE VII

Catalyst	Time(hr)	Remarks
Control	14	
2.09 g Chlorobenzene	>15	
2.4 g (0.0187 mole) Benzyl chloride	8 1/4	
12 ml Benzyl chloride + 12 ml butylamine	--	White ppt. within 5 minutes
2.2 g Chloroform	14	
12 ml Chloroform + 12 ml butylamine	>24	
3.72 g (0.0187 mole) BCMB [*]	9 1/2	
1.64 g BCMB [*]	7	0.0187 mole -CH ₂ Cl
2.46 g Benzyl Chloride + 1.37 g t-butylamine	9	pK _a =10.83 for t-butylamine
2.46 g Benzyl chloride + 1.89 g triethylamine	8 1/2	pK _a = 11.01 for triethylamine
1.64 g BCMB [*] + 1.89 g triethylamine	9	
2.46 g Benzyl chloride + 3.46 g tributylamine	9 1/2	

^{*}BCMB = 1,4-bis(chloromethyl)benzene

From this study it may be concluded that neither chlorobenzene nor chloroform catalyze the solvolysis. Benzyl chloride and 1,4-bis(chloromethyl)benzene, both with relatively labile chlorines and both capable of readily forming quaternary ammonium salts, do show catalysis. Increasing the number of -CH₂Cl groups present does not appear to increase the rate of polyester dissolution. The use of amines having pK_a^{**} values greater than that of butylamine (10.77), in addition to -CH₂Cl containing compounds, appears to have no effect.

To check the effect of ammonium salt concentration on the rate of solvolysis, the following run was made in which varying amounts of ammonium chloride were added. The results of this experiment appear to show, if anything, an increase in dissolution time with increasing ammonium salt concentration.

^{**}Negative logarithm of the acidic ionization constant

TABLE VIII

Ammonium chloride (grams)	Time(hr)
0.25	7 1/4
0.50	7 1/4
1	6 1/2
2	9
3	9 1/2
4	14 1/2

The use of bifunctional or tautomeric catalysts is well-known [19-21]. A variety of these were tried with butylamine and the polyester.

TABLE IX

Catalyst	Time(hr)	Remarks
Control	14	
12 g Cresol + 12 g BuNH ₂	13 1/2	[19]
1 g p-Aminophenol	11	[22]
1 g 8-Hydroxyquinoline	8	[21]
1 g 2-Hydroxypyridine	4	
1 g 2-Pyrrolidinone	11 1/4	[19]
1 g Maleimide	12	
1 g 2-Aminopyridine	14	[23]
1 g 2-Aminopyrimidine	14	
1 g Adenine	<10	Obscured
1 g Imidazole	11 1/2	[21]
2 g Imidazole	10	
4 g Imidazole	8	
1 g 1,2,4-Triazole	5	[20, 21]
1 g Pyrazole	6 1/4	[20]
2 g Poly(vinylimidazole)	14	[24]
1 g Poly(vinylpyrrolidone)	12	
2 g Poly(vinylimidazole)	>2 weeks	No butylamine present

The first set of data in Table IX show that (1) cresol, 2-amino-pyridine and 2-aminopyrimidine show no effect, (2) maleimide, adenine, p-aminophenol and 2-pyrrolidinone show an intermediate effect, and (3) 2-hydroxypyridine and 8-hydroxyquinoline show a marked effect. The hydroxy-substituted nitrogen-containing heterocyclics show greater catalytic activity than do the corresponding amino-substituted compounds. Further, the five membered heterocyclic compounds (imidazole, triazole and pyrazole) which are capable of acting as tautomeric catalysts show marked activity, increasing with increasing concentration (imidazole) and increasing with the proximity of the secondary and tertiary nitrogens (pyrazole more active than imidazole). The final set of data resulted from an attempt to find a "polymer effect" such as has been reported [24]. Such an effect would have, hopefully, increased the rate of catalysis (attributable to the lining-up of catalyst sites proximate to one another). Regretably, no such effect was observed.

The use of various amines was also tried again [4], but the results were generally disappointing:

TABLE X

Amine	Time(hr)	Remarks
Control	14	
1 g Guanine hydrochloride	10 1/2	
1 g 1,1,3,3-tetramethyl-1,3-butanediamine	14	
1 g N-Methylmorpholine	14 1/2	[17]
1 g Morpholine	14	[26]
1 g Pyrrolidine	14 1/2	
4 g Tetraethylenediamine	>24	[5,25]

Since it was previously observed in this study that the use of cosolvents generally decreases the rate of polymer dissolution (ref. 4 and Table V), an attempt was made to preswell the polyester samples for 24 hours prior to treatment with butylamine. It is apparent (Table XI) that preswelling the rubber in carbon tetrachloride had a marked effect on the dissolution rate. An attempt was also made to swell the catalyst, triethylenediamine, into the rubber. For this, the rubber was immersed in a

TABLE XI

Swelling Solvent	Time(hr)	Percent weight increase after 24 hr [4]
Control	14	
Carbon Tetrachloride	5	1040
Tetrahydrofuran	11 1/4	740
N,N-Dimethylformamide	11 3/4	12
1 g Triethylenediamine in 25 ml methanol	>24	13 (1 week) (Methanol alone 2)

solution of one gram of triethylene-diamine in twentieth-five milliliters of methanol and allowed to soak for a week until the sample had increased 13% by weight; methanol had previously [4] been shown to be, itself, a poor swelling agent and the major part of the swelling was attributed to the diffusion of the catalyst into the polymer matrix. The rate of dissolution was markedly decreased by this treatment. It was then decided to use a more concentrated solution for the pre-swelling (5-10 grams of triethylenediamine per 25 butylamine). This treatment caused a whitening of the rubber after one day, and on further standing caused a thusfar unexplainable degradation of the rubber to a white, amorphous mass (still insoluble in the methanol).

The following experiments, similar to those described above, involve treating one-quarter inch cubes of the polyurethane (NOL sample II) with various possible catalysts in 50 ml of n-butylamine at 50°. The results obtained were as follows: (Table XII)

TABLE XII

Catalyst	Time(days)	Remarks
Control	4	[4]
2 g Ammonium Chloride	3 1/2	
5.2 g Ammonium benzoate	4	
2.9 g Ammonium acetate	4	
3.7 g Ammonium bromide	3 1/2	
3 g Benzyl chloride	4	
2 g Cobalt (II) caproate	4	as per [13]
2 g Bismuth nitrate	3 1/4	
2 g Zinc acetonylacetate	2	
2 g Ferric acetonylacetate	3 1/4	[27]
2 g Stannous chloride	3 1/2	[29]
2 g Dibutyltin dilaurate	3	[17]
2 g 2-Aminopyridine	4	
2 g 2-Aminopiperidine	4	
2 g Imidazole	3	
2 g Guanine hydrochloride	3	
2 g 1,1,3,3-Tetramethyl-1,3-butanediamine	4	[17, 28]
2 g Triethylenediamine	3 3/4	[17, 20]
2 g Adenine	3 3/4	
1 g Poly(vinylimidazole)	4	

From this it would appear that there is only a slight increase in the rate of solvolysis when the above materials were used. The greatest increase in rate appears to have been caused by zinc acetylacetonate, while the amines and the poly(vinylimidazole) appeared to have no effect. As in the case of the polyester runs, difficulties arose from the lack of complete solubility of many of the salts and from the obscuration of a number of end-points due to the intense color of some of the solutions.

In an attempt to react both the polyester and the polyurethane with other reagents known to participate in nucleophilic attack on carbonyl groups [31], these rubbers were heated with hydroxylamine in aqueous ethanol at pH 5 for one week. No reaction was observed. Heating a one-quarter inch cube of polyester in fifty milliliters of amyl acetate at 100° was attempted in an effort to see whether a transesterification type of reaction could be caused to occur. In the presence of one milliliter of hydrochloric acid, the solvolysis was complete within one hour, but when 0.4 grams of sodium hydroxide was used instead of the acid, a white suspension resulted only after one day. Finally, in light of the reported [14] use of ammonium salts to catalyze the reaction of esters with butylamine or ammonia, a sample of polyester was treated at room temperature with a solution of two grams of ammonium chloride in twenty-five milliliters of ammonium hydroxide; no degradation was noted after one month.

The catalysis studies were now extended to the Polaris binder, IV. In a manner similar to that employed with binder III, one-quarter inch cubes of the Polaris binder IV were used in the presence of 25 ml of n-butylamine and various possible catalysts at 25°. The results of this solvolysis study are summarized in Table XIII. It should be noted that in this study, as in the catalyzed solvolysis of the polyester III, most of the compounds tested exert a catalytic effect on the rate of solvolysis. The effect of the ammonium salts on the rate of solvolysis is essentially the same as that observed in the solvolysis of the polyester III. Further, the quantity of ammonium salt used as evident from the following study, shows no clear effect on the rate of solvolysis:

<u>Grams ammonium chloride</u>	<u>Time(hrs)</u>
0.5	8
1	7
2	11
3	13 1/2
4	>14
<u>Grams ammonium perchlorate</u>	
0.25	11 1/2
0.5	11 1/2
1	11 1/2
2.2	9 1/2
3	12 3/4

TABLE XIII

Catalyst	Dissolution time(hrs)	Remarks
Control	15 1/2	Room temperature
Control	5 1/2	at 50°
1 g (0.0187 mole) Ammonium chloride	7	
1.83 g Ammonium bromide	9	
2.7 g Ammonium iodide	9 1/4	
1.44 g Ammonium acetate	8 1/4	
2.6 g Ammonium benzoate	8 1/4	
2.19 g Ammonium perchlorate	9 1/2	
1 g Tetra-n-butylammonium perchlorate	11 1/4	
1 g Tetra-n-butylammonium hydroxide	11 1/2	[32]
3.72 g 1,4-bis(chloromethyl) benzene	12	
1,3-Dibromobutane	13 1/2	
1,4-Butanediamine dihydrochloride	12	
1.92 g Sodium bromide	9	
1.53 g Sodium acetate	9 3/4	
1 g Triazole	7 1/2	
1 g Pyrazole	7 1/2	
1 g Imidazole	6 3/4	
1 g Triethylenediamine	11	
1 g 2-hydroxypyridine	9	
1 g 8-Hydroxyquinoline	9 3/4	
1 g Stannous octoate	9-10	White ppt.
1 g Dibutyltin dilaurate	9	White ppt.
1 g Zinc acetonylacetonate	9-10	White ppt.
1 g Lead acetate trihydrate	6 1/4	
1 g Bismuth nitrate hydrate	8 1/2	
1 g Zirconyl nitrate dihydrate	9 1/2	

Polyurethane binder I, when treated with fifty milliliters of n-butylamine and two grams of ammonium chloride at 50°, dissolved in less than four days. A similar sample at room temperature, though, failed to dissolve after ten days.

The dependence of solvolysis time on sample size was investigated. Cubes of binder IV were cut and placed into one-hundred milliliters of n-butylamine with either one gram of ammonium chloride or ammonium perchlorate. The following times were observed:

Sample size	Time(hrs)	Time(hrs)
	Ammonium chloride	Ammonium perchlorate
1/8 "	6	-
1/4 "	9	14
1/2 "	28 1/2	24 1/2
3/4 "	47	-
1 "	72	84

Hence, a concentrated solution of solvolyzed binder in butylamine could be made using one-inch cubes, but obviously at the expense of dissolution time. The need for a large excess of amine solvent was also indicated in the case of unplasticized rubber II, ten grams of which failed to dissolve (as one-quarter inch cubes) in fifty milliliters of butylamine after heating for over two weeks at 50°.

An attempt was made to swell sufficient butylamine into rubber IV to solvolyze the urethane bonds within the sample while the rubber was placed into a solvent capable of dissolving the fragments produced. Cubes of IV were placed, at room temperature, into butylamine (in the presence and absence of ammonium chloride) for 5.5 to 7 hours. After this time they were removed and placed into chloroform at room temperature. Although swelling was noted, the sample failed to show any dissolution.

Use of ammonium hydroxide and methylamine

Polyurethane IV was treated (as one-quarter inch cubes) with twenty-five milliliters of ammonium hydroxide, in the presence and absence of one gram of ammonium chloride, at room temperature for four days. The rubber became opaque and was slightly degraded, but was insoluble in chloroform (which was used as the criterion for estimating the extent to which crosslinks were broken). When the rubber was treated in a similar manner with aqueous methylamine for four days the resultant material was mostly soluble in chloroform. A mixture (1:1 by volume for a total volume of twenty-five milliliters) of ammonium hydroxide and aqueous methylamine at room temperature also gave a chloroform-soluble product after four days.

Samples of rubber IV were treated with 100 milliliters of concentrated ammonium hydroxide at 100° for seven days, in the presence and absence of ammonium chloride. Although both solutions became yellow, the resulting rubbers were not soluble in chloroform (even though the rubbers themselves became white and flaky).

In order to relate the results obtained here with those obtained by Tompa and French [33], solvolysis was attempted using ethylenediamine. A sample of Polaris binder IV was treated at room temperature and the dissolution times obtained were as follows:

Solution	Time(hrs)
25 ml Ethylenediamine (EDA)	12 1/2
12 ml EDA + 12 ml benzene	13-15
12 ml EDA + 12 ml benzene + 1 g ammonium chloride	13-15
25 ml EDA + 1 g ammonium chloride	18

A decrease in the rate of solvolysis was observed using both the cosolvent benzene and the "catalyst" ammonium chloride. A series of runs were then made using 2% ethylenediamine in benzene or toluene.

Sample	Temp.(°C)	Dissolution time	Comments
I	room	not dissolved after 2 wks.	in benzene
II	room	not dissolved after 2 wks.	in benzene
III	room	<5 days	in benzene
IV	room	not dissolved after 2 wks.	in benzene
II	50	not dissolved after 2 wks.	in benzene
IV	50	degraded in 12 days	in benzene
IV	100	<15 hr	in toluene
IV	100	2 days	in 2% hexylamine in toluene

At room temperature only the polyester III as previously reported [33] was affected. Ethylenediamine proved to be more efficient than hexylamine in the solvolysis of rubber IV. When polyurethane binder IV (containing no propellant) was heated for four days at 100° with toluene, in the absence and presence of one gram of ammonium perchlorate, no solvolysis was noted.

Use of acids

When a one-quarter inch cube of polyurethane binder IV was treated with twenty-five milliliters of 70% perchloric acid at room temperature, the rubber darkened and became amorphous between the fourth and seventh day of treatment. After seven days, though, the rubber still did not dissolve to any marked extent in chloroform. When 6 N hydrochloric acid was used the following results were obtained:

Sample	Temp(°C)	Dissolution time	Comments
I	room	not dissolved after 2 wks.	
II	room	not dissolved after 2 wks.	
III	room	not dissolved after 2 wks.	
IV	room	not dissolved after 2 wks.	turned dark and amorphous after one wk.
I	50°	not dissolved after 2 wks.	in 1.5 <u>N</u> -HCl
I	100°	<21 hr	
II	100°	not dissolved after 1 wk.	
III	100°	<21 hr	
IV	100°	about 50% soluble in chloroform after 4 hrs.	turned dark and amorphous after 2 hrs.

Use of ammonia

A series of runs were made using neat (25 ml) ammonia in the presence of various additives. The results may be summarized as follows:

Sample	Temp(°C)	Dissolution time(days)	Comments
IV	room	3	two 1/8" cubes; only slightly degraded
IV	room	8	two 1/8" cubes + 1 g NH_4Cl ; sol. in chloroform
IV	50°	5	1 g NH_4Cl ; sol. in chloroform
IV	50°	3	1 g NH_4ClO_4 ; dissolved
IV	50°	1	1 g NH_4ClO_4 ; insol. in chloroform
I	50°	3	1 g NH_4ClO_4 ; cracked but still intact
I	50°	6	1 g NH_4ClO_4 ; small amt. of solid, almost entirely sol. in chloroform

Sample	Temp(°C)	Dissolution time(days)	Comments
II	50°	5	1 g NH_4ClO_4 + 10 ml toluene; swollen but insol. in chloroform

Thus, all rubbers except II are solvolyzed by ammonia. Rubber IV is degraded within one to three days at 50° or within eight days at room temperature. Polyurethane I is much less reactive, taking about six days at 50°. Rubber II does not appear to be susceptible to attack by ammonia, even in the presence of a swelling agent such as toluene.

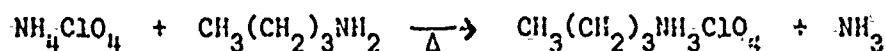
Attempted recycling

A preliminary attempt was made to reuse the products of the binder solvolysis. A mixture of five grams of polyurethane IV, twenty-five milliliters of xylene and twenty-five milliliters of ethylenediamine were heated at 50° until the rubber dissolved (19 hours). The resulting mixture was added to 250 milliliters of xylene and then 65.3 g of tolylene diisocyanate was added with cooling and stirring. A white precipitate was formed and was allowed to react for twenty-four hours. Dissolution of the white solid was attempted in dimethylformamide but was unsuccessful.

A one inch cube of binder IV was solvolyzed in one hundred milliliters of butylamine at room temperature for three days. Hydrochloric acid (6 N) was then added, until the solution was acidic to pH paper. An additional 100 milliliters of water was then added and the resulting solution was extracted three times with ether. (The acidity of the aqueous phase was checked after each extraction.) The ether extracts were then combined and extracted with dilute hydrochloric acid. The ether layer was then concentrated and a brown solid (thought to be ureas and long-chain components) was isolated. The aqueous phase was made alkaline with sodium carbonate and again extracted with ether. The second ether extract gave a small amount of brown oil on evaporation, while the aqueous phase contained not only inorganic material but rubbery globules which were subsequently found to be soluble in chloroform.

VII. Experimental - Fourth Quarter

The key objective was to study methods of solvolytically degrading propellant binders thereby making it possible to dissolve the binder fragments and/or oxidizer in suitable solvents for reclamation purposes. A solvent that will not alter the aluminum powder or AP propellant ingredients must be chosen. *N*-Butylamine, as had been shown earlier, degrades propellant binders at moderate temperatures [3]. However, it reacts with the AP to produce the less stable *n*-butyl mine perchlorate as an undesirable contaminant.



We found that other organic solvents, alcohols, and etc. do not appreciably dissolve AP or attack the binder at the moderate temperatures <50°C that we chose as safe and reasonable temperatures [3].

Workers at the Naval White Oak Laboratories reported recently that a large number of propellants and other explosives could be degraded by solvolytic techniques at higher temperatures [1, 34]. Adequate safety measures no doubt could be employed in that their lab is probably better equipped for explosive studies. The following four systems were found to be effective in degrading amide, ester, and urethane binder bonds.

1. Ethylene diamine in xylene, 0.6 to 2.0% at 115°C.
2. HCl in cyclohexanone, 1.5 N, at 115°C, or HCl in 1:1 cyclohexanone; n-propanol, 1.5 N at 115°C.
3. NH_4OH in H_2O , 1.5-6 N at 96-100°C.
4. HCl in H_2O , 1.5-6 N at 96-100°C.

In some cases separation of the AP from Al and from the binder was accomplished with a high percentage of recovery.

VII. Results and Discussion

Solvolytic Degradation

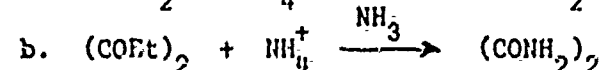
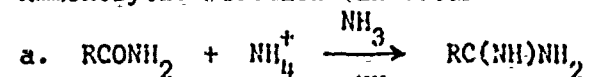
The main emphasis has been on solvent systems that promote separation at more moderate temperatures. In this report are reported our investigations on hexamethyldisilazine (HMDS) and liquid ammonia as degradation systems.

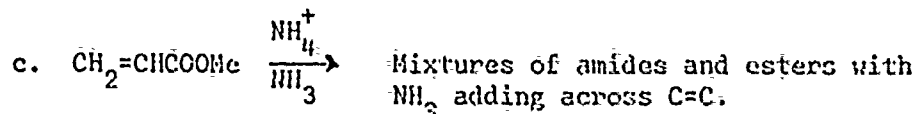
A.L. DiSalvo reported that HMDS degraded polyurethanes to give diamines and disilylethers [35]. Our results show that HMDS does degrade rocket binders but only at high temperatures. (See Table XIV)

Dilute solutions of NH_4ClO_4 (AP) in liquid ammonia at room temperature do not appreciably affect propellant binders after about two weeks of treatment. Binder degradation is accomplished at 50°C, however. The literature shows that the following chemistry of the propellant systems is important [36].

1. Amides are cleaved by ammonium salts in $\text{NH}_3(l)$.
2. Aluminum solutions in $\text{NH}_3(l)$ are less stable than those of more active metals.
3. Aluminum can react with amide ions and ammonium ions in NH_3

$$\text{Al} + \text{NH}_4^+ \longrightarrow \text{Al}^{+3} + 1/2 \text{H}_2 + \text{NH}_3$$
4. Organic compounds can undergo reduction in the presence of a dissolved metal.
5. Ammonolytic reaction can occur.





d. Relative rates are

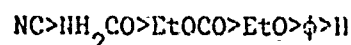
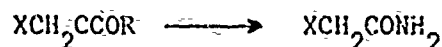


Table XIV

Degradation of Rocket Binders^a with HMDS

Binders	10% HMDS in Xylene at Room Temperature After three weeks.	10% HMDS in Xylene at 50°C After 3 weeks	2 % HMDS in Xylene at 110°C
I	No change	Only swollen	Dissolved after eight days
II	No change	Only swollen	-----
III	No change	Only swollen	Dissolved after two weeks
IV	No change	Only swollen	Dissolved after five days.

If the aluminum could be prevented from reacting or if it does not react under reaction conditions then it should be possible to reclaim the oxidizer from the propellant system by dissolving it in the NH_3 liquid.

Attempts to obtain some actual rocket propellant in order to assess some of the above reactions, were discouraged by Navy personnel. As a result, some model rocket propellant with ammonium chloride substituted for ammonium perchlorate according to the procedure as described in reference 37, was prepared. This "propellant" contained, by weight, 59.0% ammonium chloride, 12.2% aluminum powder, 0.7% by weight of triethanolamine, 12.2% of diol of molecular weight 2000, 12.0% of a triol of molecular weight 3000, 3.9% of TDI, and a few drops of D-22 catalyst. The sample, cut into 2 g cubes, was cured in a vacuum oven at 62° for 2 hours.

The initial experiment showed that at -33°C no reaction occurs between aluminum, which does not dissolve in $\text{NH}_3(l)$, and NH_4Cl at dilute concentrations in $\text{NH}_3(l)$. When the model rocket propellant is treated with liquid ammonia at 50°C for 18 hours, the propellant system is swollen and the NH_4Cl is leached into the liquid ammonia. Simple distillation of the ammonia yields about 84% recovery of the ammonium chloride. The aluminum powder remains behind in the degraded polyurethane gel, and apparently is not attacked by the liquid ammonia or the ammonium ion. Clearly more experiments are called for in this

*Toluene diisocyanate

area but the initial experiments are promising in that ammonium salts can be reclaimed from propellants in excellent yields at considerably lower temperatures than those necessary for organic solvents and also at considerably less contamination of the ammonium salts.

Photolytic Solvolysis. The solvolytic degradative approaches to reclaiming rocket fuel component parts as developed by Tompa, White and French [1, 34] and by us, which involve n-butylamine and liquid ammonia degradation, offer promise as an intermediate solution to the recovery of HEM* from current waste propellants and explosives. However, this approach is not entirely satisfactory in that:

1. relatively high temperatures, 96°-115°C, are required,
2. long reaction times of several days are necessary, and
3. although excellent yields of ammonium salts are reclaimed unavoidable contamination can occur.

Many impurities of AP, i.e. metal salts and $[\text{NiH}_2\text{ClO}_3]$ are known to greatly increase AP's sensitivity to detonation [38]. Many of these undesirable properties and results of the thermal solvolytic degradation are not present in photo solvolytic degradation. The rate of photodegradation of binders would be less dependent upon temperature. The only requirement for photodegradation of binders is that the reaction be carried out above the T_g^{**} of the binder [39]. For the elastomers employed in rocket propellants T_g is lower than room temperature [40]. Finally, solvents in which AP or other oxidizers are readily soluble may be employed [37].

Polyurethanes, polyamides, and polyesters similar to those found in propellant binders do undergo photolytic degradation [41]. A THF/polydiol linear polyurethane similar in structure to the crosslinked binder I was prepared (See Table XIV). Photolysis of this polyurethane in benzene at room temperature for only two hours gave rise to a polymer of half the intrinsic viscosity of the starting polyurethane.

A benzene solution of the sample contained in a quartz tube was irradiated with a high pressure mercury lamp for the times specified, and the intrinsic viscosities of the resulting solutions were determined using the well established procedure previously described [42]. Figure 1 summarizes this study.

Extraction Study

In the course of our studies with the polyurethane and polyester binders it was observed that some organic solvents become yellow when in contact with the polyurethanes I and IV. Since in binders I and IV a 1:1 eutectic of bis(2,2-dinitropropyl)acetal is used to plasticize the polymers it was thought that possibly the yellow color was due to the dissolution of the nitro plasticizer. An extraction study was therefore undertaken to determine the degree of plasticizer dissolution as well as to determine the most efficient solvent. In this experiment a 0.14 g sample of binder I having a 50-80 mesh particle size was placed in a Soxhlet apparatus and the extraction allowed to proceed for 24 hours. The polyurethane sample was then dried overnight at 50° in a vacuum oven and the weight loss

*High energy material; **Polymer glass transition temperature

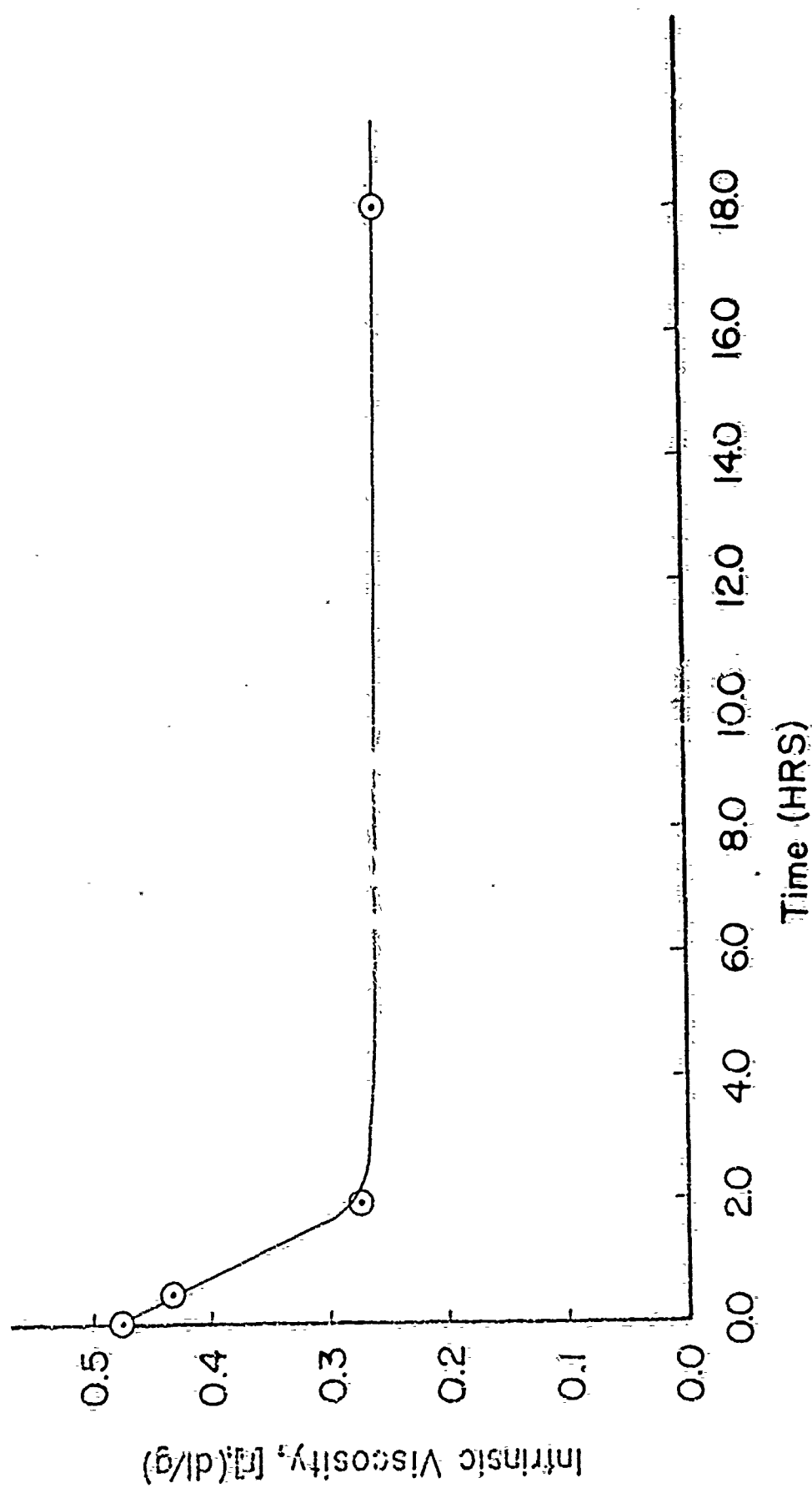


Figure 1. - "PLOT OF INTRINSIC VISCOSITY (dl/g) OF A POLYURETHANE AS A FUNCTION OF IRRADIATION TIME"

recorded. The results of this study are summarized in Table XV.

Table XV

Extraction of Binder I with Various Solvents	
Solvent	Weight loss, %
Benzene	47
Acetone	77
Methanol	81
Acetonitrile	72
Methyl Ethyl Ketone	25
Tetrahydrofuran	38
Dioxane	53
Acetic Acid	41
Dimethoxyethane	55
2-Butanol	52
Pyridine	15

The extraction study was extended to all four binders using 3-4 g samples cut into one-quarter inch cubes. Methanol was used as the solvent, the extraction allowed to proceed for 24 hours and the samples dried as previously described. The weight loss observed in these extractions as well as the weight % of plasticizer present in the binders are reproduced in Table XVI. Infrared analysis of

Table XVI

Extraction of Binders I-IV with Methanol

Binder	Wt. loss, %	Wt. % Plasticizer
I	74	75
II	46	50
III	2	0
IV	61	50

the methanol and benzene extracts from binders I and IV did not indicate methanolysis was occurring during these extractions. Although this study has not been extended to larger sample sizes or the minimum time necessary for complete extraction determined, the results are encouraging. These results suggest a simple procedure for the separation and recovery of the nitro and hydrocarbon plasticizers. In addition, this type of separation should be inexpensive and adaptable to continuous separation. Further, it can be carried out

below 64° without any foreseeable contamination of oxidizer. Furthermore, ammonium perchlorate is soluble in methanol to the extent of 2-3 g/50ml at 25° and should also be extractable. The residual binder could then be separated from the Al metal by one of the various chemical methods available. Perhaps the Ford Motor Company process [43] for hydrolyzing scrap polyurethane foam with steam at elevated temperatures could then be applied and the hydrolyzed material recovered for reuse. Unfortunately, these possibilities could not be tested due to lack of availability of actual rocket propellant.

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